Safety: Special Effects of Thermal Runaway

Chapter Heading for **Encyclopedia of Electrochemical Power Sources**

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Abstract

Any system that stores energy has the potential of becoming a significant safety problem. The objective of any designed application using a battery is to release the energy under prescribed and controlled conditions. Unfortunately, the rapid, uncontrolled release of the stored energy at the wrong time and place is a matter of concern. The presentation here addresses the special effects of thermal runaway as the phenomenon applies to batteries. Although a number of safety issues exist in the use and handling of sealed batteries, thermal runaway can be a spectacular failure mode and in recent times has garnered substantial interest and concern. As a consequence of this, a number of governmental and trade association efforts have been mounted to issue standards covering the manufacture, use and transport of batteries and battery power devices. Much remains to be done in terms of understanding the causal aspects of the thermal runaway phenomenon. Presently, the large part of the available safety guidance consists of treating the symptoms and avoiding those environmental conditions that are conducive to initiating thermal runaway.

Safety Overview

A particularly significant incident that has brought the thermal runaway problem into focus were the pictures taken with a cell phone camera of a battery induced fire in a laptop computer. The photographs are those of a laptop sitting on a table during a meeting held in Osaka, Japan. These pictures were published on the Internet and, as a consequence, brought the thermal runaway effect into the consciousness of the general public.

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14. ABSTRACT

Any system that stores energy has the potential of becoming a significant safety problem. The objective of any designed application using a battery is to release the energy under prescribed and controlled conditions. Unfortunately, the rapid, uncontrolled release of the stored energy at the wrong time and place is a matter of concern. The presentation here addresses the special effects of thermal runaway as the phenomenon applies to batteries. Although a number of safety issues exist in the use and handling of sealed batteries, thermal runaway can be a spectacular failure mode and in recent times has garnered substantial interest and concern. As a consequence of this, a number of governmental and trade association efforts have been mounted to issue standards covering the manufacture, use and transport of batteries and battery power devices. Much remains to be done in terms of understanding the causal aspects of the thermal runaway phenomenon. Presently, the large part of the available safety guidance consists of treating the symptoms and avoiding those environmental conditions that are conducive to initiating thermal runaway.

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Figure 1. Photographs of a laptop fire taken with a cell phone camera and published on the Internet.

The thermal runaway effect is a characteristic of sealed cells. This is to be distinguished from the vented flooded designs that do not exhibit this effect. As a note of caution, it is important to point out that it is possible to put a flooded cell into thermal runaway by allowing the electrolyte level to decrease to the point where one simulates a starved electrolyte environment. One can induce the thermal runway in these cases. However, the operation of that cell is well outside of its normal operating bounds.

A delicate situation exists at this point that must be appreciated by the reader. Who is responsible for the consequences of the thermal runaway? It is important to keep this point in mind if an objective assessment is to be made. There are vested interests involved here held by manufacturers, consumers and society, in general. It is important to point this out in order to establish a perspective. Clearly, objectivity is needed to understand the operational details of and to control the effect. Alternatively, advocacy positions can be taken when one attempts to establish liability for consequential damage to persons and property. The description of the thermal runaway effect can and does involve well-spun rhetoric.

Here is quote from the U.S. Consumer Product Safety Commission (CPSC) summarizing the issue. [1]

"U.S. Consumer Product Safety Commission (CPSC) staff ... has received consumer complaints and manufacturer and retailer reports involving hazards associated with batteries and battery chargers. Potential hazards include overheating, fire, electrical shock from battery chargers, thermal burns, exposure to alkaline battery electrolytes or high-velocity ejected internal components of batteries. Incidents have been reported with the battery while the product is in use, during storage and during battery charging. There have been a number of recalls involving lithium-ion batteries/battery packs/battery chargers for use in cellular telephones, portable computing products, and other personal

electronic products. There have also been a number of recalls involving other technology batteries used in products such as battery-powered ride-on toys and portable battery-powered tools."

So, "what is thermal runaway?" As a starting point, the following is offered as a place to begin. The following statement applies to VRLA batteries but, the viewpoint is actually very general and applies to virtually all sealed rechargeable batteries.

"The thermal behavior of VRLA batteries has received considerable attention in the context of both service-life and thermal runaway. Thermal runaway of VRLA batteries describes the condition where the rate of heat generation within the battery exceeds its heat dissipation capacity, and is often linked to charging abuse or high ambient operating temperatures. For batteries on float service, thermal runaway is characterized by a cooperative increase in both charging (float) current and internal battery temperature over time which may lead to catastrophic and destructive failure. Evolution of hydrogen sulfide has also been reported during thermal runaway events. System conditions believed to be conducive to thermal runaway have been described and many thermal management strategies have been advocated. The physical geometry and internal design of the VRLA battery and the design of the battery installations contribute to the susceptibility of thermal runaway. Current-limited float charging or temperature compensation of the float voltage is often proposed as important in alleviating the risk of thermal runaway. However, either technique may not be easily applied in existing standby installations. Thermal runaway may be difficult to predict and the causative agents often difficult to determine." [2]

The preceding is, in the author's opinion, a well crafted statement that serves as the basis for making two points. The first is that the statement is almost entirely descriptive. In that sense, it represents the present state of understanding of the phenomenon. Although the description is primarily focused on the VRLA battery, there are some key considerations that are common to all thermal runaway processes. The second point is that the observation is made that the effect is "...often linked to charging abuse or high ambient operating temperatures." This is an interesting observation because it seems that the user is being held responsible for the creation of the thermal runaway. It is not intended that this observation be accusatory. But, it is clear that the burden of responsibility is being placed on the user by virtue of the language being used to describe the effect. That is, it is being presumed that the battery is inherently safe and that the essential cause of the thermal runaway is abuse. This may actually be the case. Nevertheless, the claim is presumptive. The fact that the thermal runaway effect can be induced under abusive conditions does not exclude the possibility of the effect occurring during non-abusive operating conditions. The purpose here is not to point fingers to argue blame. Rather, the point of the discussion serves to indicate the lack of and the need for a fundamental understanding of the underlying mechanism together with the causal factors that bring about the thermal runaway effect.

An attempt was made within this description to relate the effect to fundamental processes. It was stated that "...thermal runaway ... describes the condition where the rate of heat

generation within the battery exceeds its heat dissipation capacity..." This is an often referenced observation that appears to provide a kind of understanding and one can get an intuitive feel for the basic effect. But there is an essential physical problem with this statement. If indeed the rate of heat generation within the battery exceeds its heat dissipation capacity, the temperature of the battery would rise to infinity. What was really meant by the statement is that the dynamic condition results in a temperature rise. Eventually a steady state is reached where the rates of heat generation and dissipation become equal. That is, at steady state, the power delivered to the battery is exactly equal to the power dissipated by the battery. Implied in this statement are the following. The battery is sealed and that it is in an overcharged condition. The latter point requires that the energy storage reactions have been fully satisfied and no further chemical energy storage can take place. In this case, the power supplied to the system is dissipated as if the battery was effectively a resistor. A battery, when being overcharged contains not only a series equivalent resistance but also a voltage gradient across the cell that must be overcome by the charging current.

So, thermal runaway is a descriptive name for a failure mode that exists in sealed batteries. It is observed by noting that the batteries continue to accept charge after they are fully charged. This excess power is converted to heat within the battery and can result in a boiling of the electrolyte. The battery surface gets very hot to the touch. This provides a sensible description of the effect.

The reason for defining the term in this way is that the response applies to all thermal runaway observations. By doing it this way, no distinction has been made between the thermal runaway effect observed in VRLA batteries as opposed to lithium ion batteries. Of course, the observed consequence of the thermal runaway in each of these batteries is quite different. However, for the purposes of this presentation, it is not desired here to imply that the triggering mechanism for the effect is different for each battery chemistry.

Thermal Runaway in Sealed Batteries

Thermal runaway in batteries has been known for quite a while. Many battery systems including nickel-cadmium, lead acid and silver-zinc have been observed to enter into a condition referred to as, "thermal runaway." The effect is normally associated with constant voltage or bus bar charging. [3]

The empirical perspective on the induction of the thermal runaway effect tends to appear as follows. During the early part of a constant voltage charge, the current decreases in a normal manner. Then as the battery approaches a full charge, the current rather than continuing to decrease, abruptly increases, heat is generated and the temperature of the battery begins to rise. The increased temperature reduces the over-potential for the irreversible gas evolution reaction (i.e., a thermally induced autocatalysis takes place). Since the applied voltage is held constant, the current continues to increase. This increased current causes additional heating that again results in a higher current draw. Thus, the thermal runaway receives its name.

A somewhat similar effect is observed during a massive short circuiting of a cell. This is induced by an external shorting of the terminals, a cell penetration usually performed using a metallic penetrator or a physical crushing of the cell.

As mentioned earlier, flooded batteries appear to be almost completely resistant to thermal runaway. Actually, the effect can be induced in flooded systems by allowing them to dry out. However, doing that means that the batteries are operating outside of their defined operational specification. In effect, one has intentionally or inadvertently, converted a flooded cell into a starved electrolyte cell.

Manifestations of Thermal Runaway

The burning laptop shown above is a reminder of the consequences of thermal runaway. In the case of aqueous based electrolyte systems, the effects range from steam being generated to severe battery case distortions and an occasional detonation. Although these effects are rare, they have been observed.

The valve regulated lead-acid battery in thermal runaway will reach only a relatively moderate internal temperature (i.e., that of the boiling electrolyte) at which point the battery vents steam. Since the separator is made of glass, it is unaffected by this relatively low temperature excursion. The loss of water caused by the venting eventually reduces the conductivity between the battery plates to a sufficiently low level that the battery ceases to accept further charge. The battery then cools slowly. During the high temperature excursion, the internal cell environment accelerates irreversible processes that often are not a concern at normal operating temperatures. One very prominent effect is the reduction of sulfuric acid by metallic lead resulting in the generation of hydrogen sulfide.

The high temperature excursion has resulted in some failures that are shown in the following figures.

Figure 2 shows the residual consequences of a battery detonation that accompanied an attempt to exercise a standby power generator. The white material is baking soda that was used to neutralize the scattered battery electrolyte. The detonation was audible and the fragmentation is evident. In the reference cited, a web page was dedicated to reported personal experiences relating to battery detonations. [4] These are rare events and the weight of the documentation helps to establish the effect as a matter of concern.

Since these are relatively rare events and have not been, as yet, adequately reproduced for laboratory study, some interesting speculation has been offered. Clearly, the detonation of some batteries has been reported. The graphics suggest that a rapid hydrogen-oxygen recombination has taken place. Also, the high temperatures can result in the softening of the plastic containers together with a pressurization caused by boiling electrolyte could have caused the observed swelling and venting as shown in Figures 3 and 4. There is also the possibility that the two effects occur concurrently. As was mentioned earlier, these are very rare events and are difficult to reproduce under laboratory conditions.



Figure 2. Consequence of a VRLA battery detonation. [4]



Figure 3. Battery deformation that resulted from a thermal runaway. [5]



Figure 4. Thermal runaway consequence as observed by the author.

NiCd Discussion

A somewhat special situation exists during the thermal runaway of a nickel cadmium battery that distinguishes it from that of a VRLA battery. During the thermal runaway of a NiCd battery, the battery may get so hot that the battery separator melts allowing the plates to physically come in contact with each other. The plastic cell containers also melt permitting ground shorts with an outside steel support member. The consequence of this is that the battery may catch fire, explode, or the result in a local arcing. The latter effect may burn holes in the outer stainless steel box and surrounding structures. For this reason, the nickel cadmium batteries are often equipped with temperature sensors that are integrated into temperature warning systems. The documented reports of NiCd thermal runaway appear largely in aircraft applications.

Wide Need for Portable Applications, Laptops, HEVs, etc.

There is a growing concern regarding the thermal runaway effect in view of the escalation of the number of applications using sealed batteries. The demand for laptops and cell phones that employ sealed batteries have achieved such high volumes that the occasional thermal runaway failure appears. The advent of the higher energy containment envisioned in Hybrid Electric Vehicle applications has let to the development of safety standards for battery applications.

Approaches for Control

Almost without exception, safety circuits are built into Li-ion cells and batteries to prevent electrical abuse. In rare events, Li-ion batteries in both laptops and phones have been known to spontaneously self-heat with various consequences. These events have lead to product recalls.

Using an organic electrolyte in lithium ion cells that is in physical contact with powerful oxidizing and reducing agents relies on slow chemical kinetics for achieving cell stability. This enables the existence of a high energy storage capability. Battery monitoring is absolutely essential for safe application. The aqueous based electrolyte cells begin with a relatively inert solvent that limits the temperature excursion by employing the liquid to gas phase change as a means for limiting the high temperature excursion. Nevertheless, the heat dissipation that is the consequence of the delivery of the stored electrical energy needs to be taken into consideration.

As a consequence, large energy storage applications designed for higher power delivery require built-in cell and module monitoring, power management, power conditioning, power shutdown circuits, change and discharge control, over- and undercharge protection, cell equalization and thermal management subsystems.

Need and Development of Standards

It is well-known that the demand and use of batteries in consumer products continues to grow at an ever increasing rate. The proliferation of these batteries has led manufacturers to increase battery operating duration while reducing the component size and weight. This naturally led to implementing battery chemistries that package ever increasing energy content in smaller containers. High energy chemistry batteries that include lithium ion and lithium polymer designs are thinner, smaller, and lighter weight and store more energy than traditional aqueous electrolyte rechargeable batteries. While conventional battery chemistries, such as lead acid, pose fire and explosion hazards that must be considered, the combination of high energy packed into a small volume and more energetic chemistries requires special safeguards to minimize the potential hazards. Batteries having larger stored energy capacities often need additional safety circuits and increased operational care when using and handling. In addition, batteries must be properly tested with the ultimate application and battery charger as an integrated system.

The widespread recall of laptop batteries in 2006 affected nearly 10 million products from five major manufacturers. Several standards developers continue to look at possible solutions to help alleviate manufacturing faults and improve battery safety. What follows is a short discussion of some of the efforts currently underway.

Batteries for Portable Computing

In November 2006, the Institute of Electrical and Electronics Engineers (IEEE) began to build improved measures into its existing lithium ion standard.

Updates to IEEE 1625 - Standard for Rechargeable Batteries for Portable Computing aim to make laptop battery systems more reliable and robust by improving their overall performance.

Lithium Ion Batteries

The Underwriters Laboratories (UL) worked with laptop and battery manufacturers to upgrade UL 1642 - Lithium Batteries that was submitted to the American National Standards Institute (ANSI) for approval in September 2006.

The proposed scope of the new standard presents requirements that are specifically intended to reduce the risk of fire or explosion and resulting injury to persons. Supporting this effort, three UL task groups proceeded to look at ways for introducing relevant component requirements, production line testing specifications and lithium battery pack requirements into the standard.

In addition, UL is seeking input from its lithium battery standards technical panel and standards subscribers on the coordination of UL 1642 with related ANSI and International Electrotechnical Commission (IEC) standards. Further, UL representatives indicated that they will increase the frequency of its audits of battery manufacturers and take steps to improve its auditor training program.

The Information Technology Industry Council (ITIC) reviewed and integrated its company-specific standards from laptop makers into a single list of recommended requirements. This list shall be shared with UL as input into the 1642 update. The objective of this effort is to resolve varied and inconsistent protocols among laptop manufacturers.

The ANSI C18 Accredited Standards Committee has long been concerned with the development of standards for lithium ion batteries. The group is updating its current standard, ANSI C18 - 2M - Part 2 for Portable Rechargeable Cells and Batteries - Safety Standard.

The National Electrical Manufacturer's Association (NEMA), the ANSI subcommittee on safety standards - C18-5 - has been following developments related to the recent lithium ion battery recalls and is preparing itself for revising its battery safety standard.

Quality Control Standard for Testing Cells

The Association Connecting Electronics Industries (IPC) is developing a quality control standard for testing cells. IPC entered the lithium ion manufacturing activity in August

2006, with a newly formed group led by IPC's established original equipment manufacturer (OEM) Critical Components Committee.

In October 2006, the IPC Lithium Ion Battery Subcommittee, that represents both the major laptop manufacturers and independent research and development firms in the portable power industry, met to organize its standard. This standard shall cover process requirements, quality control and assurance for lithium ion battery cells.

Electric and Hybrid Electric Vehicle Power Source Testing

In view of the need for better specification of the battery application in Hybrid Electric Vehicles, the definition and specification of abuse test protocols have been established. These protocols serve to simulate actual use and abuse conditions that may take place outside the expected safe operating limits of electric and hybrid electric vehicles in terms of their electrical energy storage systems. These tests provide a common framework for abuse testing various electrical energy storage systems incorporating improvements and refinements to test descriptions presented in the Society of Automotive Engineers Recommended Practice SAE J2464 "Electric Vehicle Battery Abuse Testing." [6]

Concluding Remarks

Although a number of safety issues exist in the use and handling of sealed batteries, thermal runaway is a spectacular failure mode that has garnered substantial interest and concern in recent times. As a consequence of this, a number of governmental and trade association efforts, both domestic and international, have been mounted to issue standards covering the manufacture, use and transport of batteries and battery power devices. There remains a need to harmonize the standards that are already in place. Much remains to be done in terms of understanding the causal aspects of the phenomenon. A large part of the focus of the safety guidance remains that of treating the symptoms and avoiding those environmental conditions that are conducive to thermal runaway initiation.

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- 4. http://www.rayvaughan.com/battery_safety.htm

- 5. C. Michael Hoff and Kenny Steeves,"New Insights into Thermal Runaway of Valve Regulated Lead-Acid Batteries," BATTCON 2005, May 2-4, 2005, Miami Beach, FL.
- 6. Daniel H. Doughty,"FreedomCAR, Electrical Energy Storage System, Abuse Test Manual for Electric and Hybrid Electric Vehicle Applications," SAND 2005-3123, Sandia National Laboratories, June 2005

Further Reading:

International Standards and Testing Applicable to Batteries - Listing of the most common standards and the organizations that issue them

http://www.mpoweruk.com/standards.htm

Plan of Action to Address Battery safety Concerns – U.S. Department of Transportation

http://safetravel.dot.gov/Action_Plan.pdf

MCO 5100.8, Marine Corps Occupational Safety and Health Program Manual, CHAPTER 17

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